

PATENT SPECIFICATION

NO. DRAWINGS

Inventors: ERIC VERO and JAMES NORMAN VICKERS

1022.733



1022.733

Date of filing Complete Specification Feb. 4, 1965.

Application Date May 19, 1964.

No. 20508/64.

Complete Specification Published March 16, 1966.

© Crown Copyright 1966.

Index at acceptance:—C2 C(2A2, 2A13, 3A13B2C, 3A13B2F5)

Int. Cl.:—C 07 c

COMPLETE SPECIFICATION

Triaminobenzene

We, WHIFFEN & SONS LIMITED, a British Company, of Willows Works, Derby Road, Loughborough, Leicestershire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the formation of triamines by the reduction of trinitrobenzene or trinitrobenzoic acid.

The starting materials used in the preparation of phloroglucinol or symmetrical trihydroxybenzene are the trinitrobenzene compounds such as symmetrical trinitrobenzene and trinitrobenzoic acid. To obtain phloroglucinol the trinitrobenzene compound is first reduced to triaminobenzene which is then hydrolysed to give the desired product. If trinitrobenzoic acid is used decarboxylation takes place during reduction.

The present invention is concerned in general with an improved process for reducing symmetrical trinitrobenzene or trinitrobenzoic acid to triaminobenzene which may be hydrolysed to give phloroglucinol.

It has been proposed to reduce trinitrotoluene to triaminotoluene in the presence of iron and water employing a small quantity of acid relative to the amount of iron. The quality of the product however left much to be desired and a modified process was later proposed in which symmetrical trinitrobenzene compounds were reduced with particles of iron keeping the acidity very high in order to stabilize the amino compound against oxidising agents.

It has now surprisingly been found that trinitrobenzene or trinitrobenzoic acid compounds can be successfully reduced by iron filings in the presence of a catalytic amount of acid and/or a salt or salts derived from a

strong acid if the trinitrobenzene compound is added to the reduction mixture as a solution.

Accordingly the present invention provides a process for reducing trinitrobenzene and trinitrobenzoic acid to triaminobenzene wherein a solution comprising trinitrobenzene or trinitrobenzoic acid is gradually added to a suspension of iron powder in a solution comprising a strong mineral acid and/or a salt or salts derived from a strong acid. The solution comprising the trinitrobenzene compound may be obtained by dissolving the trinitrobenzene compound in a weak alkali, water, an organic solvent or a mixture of water and an organic solvent. If a weak alkali is used to dissolve the trinitrobenzene compound a stoichiometric amount of acid is simultaneously added to the suspension of iron powder. The solvent for the acid and/or salt or salts derived from a strong acid may be water or a mixture of water and an organic solvent.

The process of the present invention is particularly applicable to the reduction of symmetrical trinitrobenzene or trinitrobenzoic acid to symmetrical triaminobenzene. The resulting triaminobenzene may be concentrated to obtain the free base by crystallisation or it may be obtained after concentration as its hydrochloride by precipitation with hydrochloric acid but its main use is that of an intermediate in the production of phloroglucinol. In a modification of the present invention therefore a solution comprising symmetrical trinitrobenzene or trinitrobenzoic acid and either a weak alkali, water, an organic solvent or a mixture of water and an organic solvent, is gradually added to and reacted with a suspension of iron powder in a solution comprising an acid/or a salt of a strong acid and, after filtration, the product

BEST AVAILABLE COPY

is hydrolysed to phloroglucinol by any of the known methods. For example the filtrate may be acidified and heated to effect hydrolysis of the triaminobenzene.

5 The organic solvent used in the process of the invention should be one which is miscible with water in all proportions in which it is to be used and which further more does not form an azeotrope with water. The water/10 solvent mixture should be one in which both products and reactants are soluble. The organic solvent preferred above all others is acetone but other solvents such as ketones, aldehydes, esters, ethers or alcohols may also be used.

15 The temperature at which the process of the invention is operated may be varied in a wide range but higher temperatures naturally favour a more rapid reaction. Temperatures in the range 70—90°C may be employed; preferably temperatures in the range 80—85°C at normal pressures are employed.

20 The temperature of the reaction mixture is advantageously controlled by maintaining the reaction mixture at boiling point and refluxing the distilled solvent. By adjusting the composition of, for example an acetone/water mixture, temperatures in the range 56°C upwards may be obtained. Suitably an acetone/water mixture is used in the process of the invention the composition of which is such that the reaction mixture can be refluxed at a temperature in the range 80—85°C. The composition of the acetone/water35 mixture is preferably 10% by volume acetone in water. For a given acetone/water composition the temperature at which the mixture boils and therefore at which the reaction is performed can be further controlled by adjusting the pressure under which the reaction takes place.

40 The reduction reaction is preferably carried out in the presence of an excess of the reducing agent. Such an excess may be obtained by adding the trinitrobenzene compound, possibly as a solution in acetone, in small proportions to the reducing agent. Such additions of the trinitrobenzene compound are suitably made over a period of time varying from two to four hours, preferably over a period of not less than three hours.

50 The iron powder used in the reduction should be as fine as possible and it is advantageously etched by a preliminary acid treatment. It is preferred to use iron powder which will pass a 140 B.S. mesh sieve.

55 The pH of the reaction mixture depends on whether an acid or a salt of a strong acid is used. If an acid is used as the catalyst the pH of the filtered reaction mixture varies in the range 4.0 to 6.0 at the beginning of the reduction to 6.0 to 8.0 at the end of the reduction. Typically the pH will be in the region 5.5 at the beginning of the reduction and in the region 7.0 at the end of the reduc-

tion. If the reaction is catalysed by the salt of a strong acid the pH of the filtered reaction mixture varies from 7.0 at the beginning of the reaction to 9.0 at the end of the reaction.

70 As an acid catalyst hydrochloric acid may be used and is preferably used in quantities such that at the end of the reduction the pH of the mixture is still acid, for example in the range 6.5 to 7.0. More acid is undesirable since it causes partial hydrolysis of the amine.

75 It is only necessary to use the acid or a salt of a strong acid in catalytic amounts.

80 In a specific embodiment of the present invention a 10—30% solution of symmetrical trinitrobenzene or trinitrobenzoic acid in acetone is fed into a reaction vessel containing a suspension of iron powder in a solution of composition—acetone 8.0 to 9.0 v/v water 85 91—92% and hydrochloric acid 0.2%.

The trinitrobenzene is added to the reaction vessel over a period of three hours during which the contents of the reaction vessel are thoroughly agitated and heated to a temperature of 80—85°C, the solvent vapours being refluxed. The molar ratio of the trinitrobenzene compound/iron/acid used is 1/22.5/0.2. At the end of three hours the reaction mixture containing triaminobenzene is filtered and acid, preferably hydrochloric acid, is added to the filtrate which is refluxed for twenty hours and then concentrated. Phloroglucinol is then crystallized out by cooling the reaction mixture.

100 The following example is given by way of illustration of the process of the present invention:

A reducer was charged with the following ingredients:

Water	130 gallons
Commercial hydrochloric acid (36° Tw)	9 lbs.
140 mesh iron powder	530 lbs.
Acetone	12 gallons

110 The mixture was heated to boiling point (80°C) and a solution of 112 lbs trinitrobenzoic acid was fed into the reducer over a period of three hours maintaining the reaction temperature at 80—85°C and refluxing the distillate. The mixture was thoroughly agitated throughout the reaction period.

115 After completing the addition of the trinitrobenzoic acid the sludge was allowed to settle and the liquid was decanted off. The sludge was then washed with water and filtered. The decanted liquid was filtered and the two filtrates combined. The combined filtrate containing triaminobenzene was then acidified to a pH 2 with hydrochloric acid 120 and refluxed at 100°C for twenty hours. Phloroglucinol was obtained by concentration and crystallization.

WHAT WE CLAIM IS:—

1. A process for reducing trinitrobenzene or trinitrobenzoic acid to triaminobenzene wherein a solution comprising a trinitrobenzene or trinitrobenzoic acid is gradually added to a suspension of iron powder in a solution comprising a strong mineral acid and/or a salt or salts derived from a strong acid. 25
2. A process as claimed in claim 1 wherein the trinitrobenzene compound is symmetrical trinitrobenzene or trinitrobenzoic acid. 30
3. A process as claimed in claim 1 or claim 2 wherein the solution comprises trinitrobenzene or trinitrobenzoic acid and an organic solvent. 35
4. A process as claimed in claim 3 wherein the solution also contains water.
5. A process as claimed in claim 3 or claim 4 wherein the solvent is a ketone, aldehyde, ester, ether or alcohol.
6. A process as claimed in claim 3 or claim 4 wherein the solvent is acetone.
7. A process as claimed in any of the preceding claims when carried out at a temperature of 70—90°C.
8. A process as claimed in any of the preceding claims wherein the acid is hydrochloric acid.
9. A process for reducing trinitrobenzene or trinitrobenzoic acid substantially as hereinbefore described.
10. A process for preparing phloroglucinol from trinitrobenzene or trinitrobenzoic acid substantially as hereinbefore described with reference to the example.
11. Aminobenzenes when prepared by the process as claimed in any of claims 1 to 9.
12. Phloroglucinol when prepared by the process as claimed in claim 10.

F. MURPHY,

Agent for the Applicants,
Chartered Patent Agent,
Fisons Limited, Harvest House,
Felixstowe, Suffolk.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1966.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.